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Sensitization of photoconductive polyimides for photovoltaic applications

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Abstract

Soluble polyimides based on the N,N′-bis-(4-aminophenyl)-N,N′-diphenylbenzidine with a linkage between the phtalimide groups X = O , - , SO_2 , CO are investigated for their photovoltaic properties. Sensitization of these photoconductive polyimids with different small molecules like Rhodamine 6G as well as [6,6]-phenyl-C_{61}-butyric-acid-methyl-ester (PCBM) is demonstrated by current / voltage and spectrally resolved photocurrent spectroscopy.

Keywords: Polyimides, organic photovoltaics, bulk heterojunction, fullerenes and derivatives, spectral photocurrent spectroscopy

1. Introduction

Aromatic polyimides are highly thermostable polymers with excellent mechanical and dielectric properties that form strong films and layers on different substrates with interesting properties for photovoltaics [1] and electroluminescence [2].

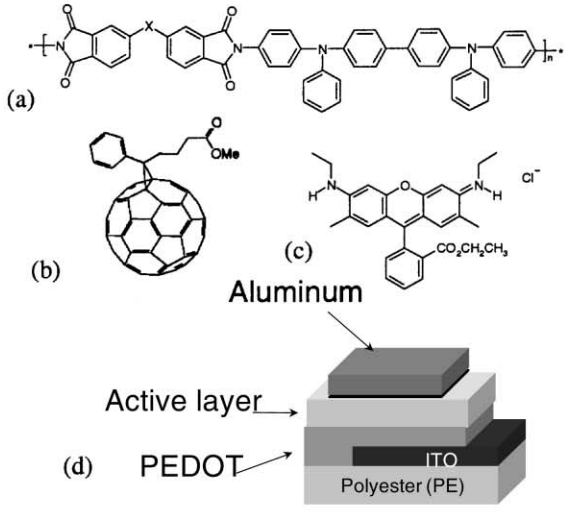

Fig. 1: (a) Structure of investigated Polyimides, with X = SO_2, -, CO, O; Structure of (b) PCBM and (c) Rhodamine 6G; (d) Device Scheme

The polymer chains of these aromatic polyimides consist of alternating electron acceptor and electron donor fragments. In the polyimides studied (Fig. 1) two triphenylamine (TPA) units as donor fragments are linked to one electron accepting diimide unit.

Partial charge transfer occurs (from TPA to the diimide group) along the chain and is stabilized by a charge transfer complex with the neighbour chain. The doubled donor unit leads to structures in the bulk that should favour charge transfer along the chain and charge carrier transport vertical to the chain at the same time [1].

2. Experimental

Solutions of polyimide , PCBM and Rhodamine 6G in tetrachloroethane and mixtures of the latter two with polyimide (X = SO_2) were characterised by absorption measurements on a HP spectrometer and luminescence measurements on a Hitachi F-4010 Luminescence Spectrophotometer.

The photovoltaic devices (Fig. 1d) [3] were prepared on PE/ITO substrates with a PEDOT layer between the ITO and the photoactive polyimide layer. The Al top electrode was thermally evaporated with ~ 80 nm.

The photoactive films were cast from solutions of the polyimides in tetrachloroethane (c = 1,5 wt./vol %) by doctorblading at 60°C. For the sensitized devices 6,6′-PCBM (c = 1,5 wt./vol. %) (Fig. 1b) or Rhodamine 6G (c =

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0,15 wt./vol. %) (Fig. 1c) or both of them were mixed to the polyimide (SO_2) solution. Thin films were again cast under identical conditions.

The active area of all devices was 5 mm^2 and I/V measurements were carried out at 80 mW/cm^2 on a Steuernagel solar simulator with a Keithley 2400 source measurement unit.

3. Results and Discussion

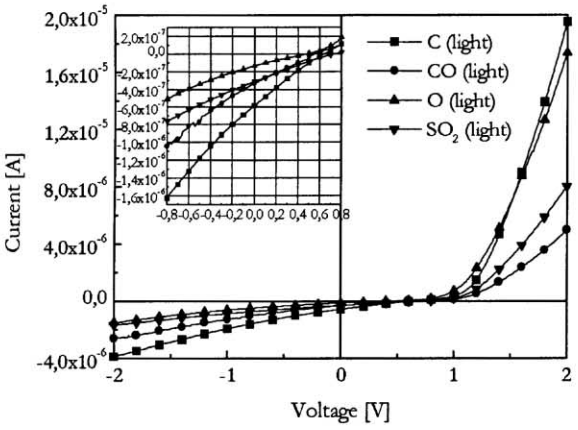

Fig. 2: I/V curves at AM 1.5 of PV devices with pristine polyimide.

The I/V measurements of PV devices from the four different pristine polyimides are shown in Fig. 2. These materials show the expected photoeffect, while diode behaviour is rather poor.

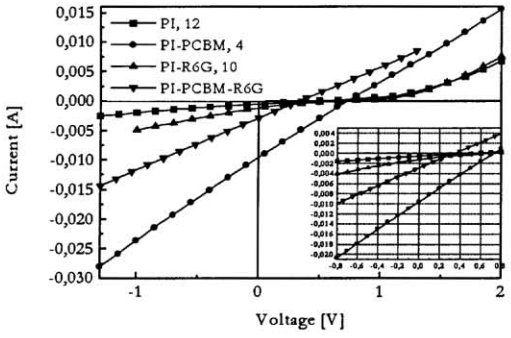

Fig. 3: I/V measurements under AM 1.5 of PV devices with pristine and sensitized Polyimide (SO_2).

Fig. 3 shows the I/V measurements of a device from pristine polyimide (SO_2) in comparison to the same polyimide (SO_2) devices sensitized with PCBM, Rhodamine 6G and PCBM/Rhodamine 6G. A clear enhancement of the photovoltaic effect with respect to the short circuit current is observed for all sensitized devices (Table 1), while diode behaviour is still poor. Best efficiencies were reached for the PCBM sensitized diodes.

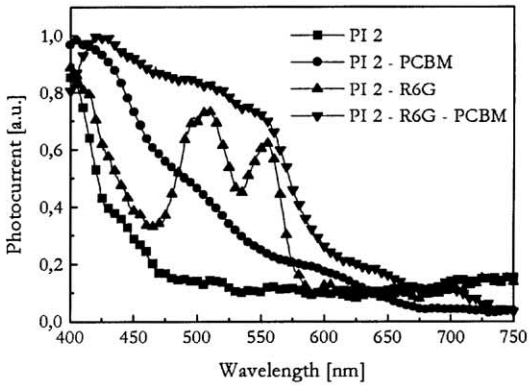

Fig. 4: Spectrally resolved photocurrent (corrected to cal. Si diode) of polyimide and polyimide / sensitizer devices normalized to their peak .

In Fig. 4 the spectrally resolved photocurrent for the sensitized devices in comparison to a pristine polyimide (SO_2) device is shown. For both sensitizers, Rhodamine 6G as well as PCBM, a spectral sensitization according to their absorption is observed. For the pristine polyimide, a weak shoulder around 450 nm may indicate the absorption band due to the charge transfer complex between the neighbour chains [1].

	Voc[mV]	I_{sc}[μA/5mm^2	η_{eff}
PI (SO_2)	525	0,0543	0,0016
PI (SO_2)/PCBM	725	9,57	0,042
PI (SO_2)/R6G	725	1,19	0,004
PI (SO_2)/R6G/PCBM	325	2,86	0,006

Table 1: Power characteristics of several PI devices illuminated with 80 mW/cm^2 from a solar simulator.

4. Conclusion

The polyimides studied with double TPA donor units can be sensitized by various strategies. One possibility is the use of small molecular dyes which increase the I_{SC} by a factor of ~10 under AM1.5 in the case of Rhodamine 6G. Another way is the use of electron acceptors such as 6,6´-PCBM. This sensitizer increases the I_{SC} under AM1.5 by a factor of ~100. The overall AM1.5 efficiency of <0,1 % is limited by the transport properties of the polymer matrix. Further improve of the transport properties is necessary to enhance the PV performance.

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